

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 7/50	A1	(11) International Publication Number: WO 99/05253 (43) International Publication Date: 4 February 1999 (04.02.99)
(21) International Application Number: PCT/US98/13480 (22) International Filing Date: 29 June 1998 (29.06.98) (30) Priority Data: 08/900,800 25 July 1997 (25.07.97) US (71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (72) Inventors: WEIDMAN, David; 11 Village Circle, Mendham, NJ 07945 (US). MCDONOUGH, George; 41 South Road, Mendham, NJ 07945 (US). THOMAS, Raymond; 5990 Hopi Court, Pendleton, NY 14094 (US). SHANKLAND, Ian; 200 Forest Hill Drive, Williamsville, NY 14221 (US). ROBINSON, Roy; 38 Andrews Avenue, Cheektowaga, NY 14225 (US). SWAN, Ellen; 27 Whitestone Lane, Lancaster, NY 14086 (US). (74) Agents: CRISS, Roger, H. et al.; AlliedSignal Inc., Law Dept., 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CLEANING VAPOR COMPRESSION SYSTEMS (57) Abstract <p>Cleaning a component of a vapor compression system with a cleaning composition having a hydrofluorocarbon as an active ingredient.</p>		

CLEANING VAPOR COMPRESSION SYSTEMS

FIELD OF INVENTION

5 The present invention relates to cleaning lubricated vapor compression systems. More specifically, this invention relates to removing lubricants from such systems by the use of a hydrofluorocarbon.

BACKGROUND OF THE INVENTION

10 There is a need to clean lubricated vapor compression systems and their components during manufacture and service.

Vapor compression systems are well known in the art. They are used in a wide variety of applications such as heating, air conditioning, and refrigeration. By compressing and expanding a heat transfer agent or refrigerant, these systems absorb and release heat according to the needs of a particular application.

15 Common components of a vapor compression system include: vapor or gas compressors; liquid pumps; heat-transfer equipment such as gas coolers, intercoolers, aftercoolers, exchangers, economizers; vapor condensers, such as reciprocating piston compressors, rotating screw compressors, centrifugal compressors, and scroll compressors; evaporators; liquid coolers and receivers;

20 expanders; control valves and pressure-drop throttling devices such as capillaries; refrigerant-mixture separating chambers; steam-mixing chambers; and connecting piping and insulation. These components are typically fabricated from copper, brass, steel and conventional gasket materials.

25 Since vapor compression systems have sliding, rotating or other moving components, most require the use of a lubricant which is mixed with the refrigerant. There is a need from time to time to clean such systems and their

components by removing the lubricants from their surfaces. Such a need arises, for example, during the retrofit of a chlorofluorocarbon (CFC) or hydrochlorofluorocarbon (HCFC) refrigerant to a hydrofluorocarbon (HFC) refrigerant, and during service, especially after a catastrophic event such as compressor burnout. There is also a need to clean such systems during manufacture.

Until recently, chlorofluorocarbons (CFCs), such as trichloromethane (R-11), were used as cleaning agents for such systems. Although effective, CFCs are now considered environmentally unacceptable because they contribute to the depletion of the stratospheric ozone layer. As the use of CFCs is reduced and ultimately phased out, new cleaning agents are needed that not only perform well, but also pose no danger to the ozone layer.

A number of environmentally acceptable solvents have been proposed, but their use has been met with limited success. For example, organic solvents, such as hexane, have good cleaning properties and do not deplete the ozone layer, but they are flammable. Aqueous-based cleaning compositions have zero ozone depletion potential and are non-flammable, but they tend to be difficult to remove from the cleaned surfaces due to their relatively low volatility and the presence therein of additives that leave a residue. Additionally, aqueous-based cleaning compositions are often inadequate for cleaning typical organic soils that are present in vapor compression systems. Terpene-based solvents, like aqueous-based cleaning compositions, are difficult to remove from the system.

Therefore, a need exists for the identification of environmentally-acceptable cleaning agents that effectively clean vapor compression systems. The present invention fulfills this need.

DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The present invention provides for the effective cleaning of lubricated vapor compression systems using a hydrofluorocarbon (HFC) while posing no risk to the ozone layer.

5 One aspect of the present invention relates to a cleaning composition comprising an HFC or a combination of HFCs. The applicants have found that HFC-based cleaning compositions have a number of attributes or properties that render them effective in cleaning vapor compression systems. First, a suitable HFC-based composition has adequate miscibility with commonly used lubricants,
10 such as mineral oils, polyalkylene glycols, and polyol ester oils, to effect their removal from the surfaces that need to be cleaned. The term "adequate miscibility" as used herein refers to the composition's ability to interact with a lubricant to form a solution, emulsion, suspension, or mixture under normal cleaning conditions. Second, a suitable cleaning composition has a combination of properties that
15 enables it to be easily and completely removed from the treated surface. To this end, it should evaporate readily using conventional techniques known in the art such as flushing the system with nitrogen or other inert gas, pulling a vacuum in the system, and/or heating the system. Third, a suitable cleaning composition has little or no flammability within the temperature ranges for which it is used. This means
20 it should have no flash point up to its approximate boiling point. Fourth, it is compatible with all components and materials used in vapor compression systems including metals and sealants. And fifth, a suitable HFC composition poses no threat to the ozone layer.

 In addition to these properties, a preferred cleaning composition has a
25 volatility suitable for use in a vapor degreaser. That is, the volatility should be high enough such that the composition can be vaporized readily to produce a condensing vapor, but low enough such that the composition can be contained in a

conventional open or closed degreaser. The more preferred embodiment of the composition has a volatility low enough such that the composition remains substantially a liquid at about room temperature.

5 A more preferred embodiment of the composition also has an atmospheric lifetime such that it contributes to neither smog nor the greenhouse effect. This means that the atmospheric lifetime should be long enough to allow it to escape from the lower to the upper atmosphere and avoid contributing to smog formation, but not be so long that it contributes to greenhouse warming. A preferred HFC
10 should have an atmospheric lifetime of between about 1 and about 100 years, and preferably between about 1 and about 50 years, and more preferably between about 2 and about 15 years.

Suitable HFCs used in the cleaning composition include those, which, individually or in combination with other composition constituents, impart the aforementioned properties to the composition.

15 Among the more important properties imparted to the composition by the HFC is suitable volatility to evaporate readily and completely from the treated surface. Factors that affect evaporation include vapor pressure, the rate at which heat is applied, the heat conductivity of the liquid, specific heat of the liquid, latent heat of vaporization, surface tension, molecular weight, rate at which the vapor is
20 removed, vapor density of the solvent, and humidity of the solvent (*see* B.P. Whim and P.G. Johnson, *Directory of Solvents* 34 (*Blackie Academic & Professional (an Imprint of Chapman and Hall)*, 1996). The cooperation of these factors and their effect on evaporation tends to be complex, however, the following equation provides a simple relative measurement:

$$25 \quad R_E = 0.8217 P_m \times (MW)^{1/4} \quad (1)$$

where R_E is the evaporation index, and P_m is the vapor pressure in mm of mercury at room temperature? (J. John Stratta, Paul W. Dilion, Robert H. Semp, Tables of Solubility Parameters, Union Carbide Chemicals and Plastics, 50-647 *J. of Coatings Technology* 37-49 (Dec. 1978). The evaporation index is a relative measurement based on n-butyl acetate, wherein n-butyl acetate's index is 100. Exemplary evaporation indexes are provided for selected compounds in Table 1 below.

TABLE 1 -- Evaporation Rates for Selected Compounds

Compound	Evaporation Rate
trichlorofluoromethane	7732
1,1,2-trichlorotrifluoroethane	3815
2,2-dichloro-1,1,1-trifluoroethane	7052
1,1-dichloro-1-fluoroethane	5337
1,1,1,3,3-pentafluoropropane	10411
1,1,2,3-tetrafluoropropane	3832
1,1,2,2,3-pentafluoropropane	7230
1,1,1,2,3-pentafluoropropane	7528
Propane	38927
Water	82

It has been found that a suitable HFC has an evaporation index of between about 1,000 and about 20,000. In a preferred embodiment, the evaporation index ranges from about 2,000 to about 11,000.

Another important attribute imparted to the composition by the HFC is non-flammability. As mentioned above, the composition should not have a flash point up to its approximate boiling point. To this end, a suitable HFC has a sufficient concentration of fluorine atoms such that the ratio of the atomic weight of all the fluorine atoms to the molecular weight (M.W.) of the total molecule is greater than about 0.65. Exemplary HFCs of this preferred embodiment include,

for example, tetrafluoropropanes, pentafluoropropanes, hexafluoropropanes, hexafluorobutanes and heptafluorobutanes.

It is also preferable that the HFC include tetrafluoropropanes or pentafluoropropanes having at least one fluorine atom on each of their two terminal carbon atoms. Exemplary HFCs of this preferred embodiment include, for example, 1,1,2,2,3-pentafluoropropane (HFC-245ca), 1,1,2,3,3-pentafluoropropane (HFC-245ea), 1,1,1,2,3-pentafluoropropane (HFC-245eb), 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,3,3-tetrafluoropropane (HFC-254fa), and 1,1,1,3-tetrafluoropropane (HFC-254fb).

The more preferable HFCs include HFC-245ca, HFC-245ea, HFC-245eb, HFC-245fa, and HFC-254fb.

The HFC(s) can be produced using known equipment, methods and techniques. For example, a method of producing HFC-245fa is taught in U.S. Patent No. 5,574,192. The process first involves reacting CCl_4 and vinyl chloride in the presence of a telomerization catalyst under conditions which produce a compound of the formula $\text{CCl}_3\text{CH}_2\text{CHCl}_2$. Next, this compound is reacted with hydrogen fluoride in the presence of a fluorination catalyst under conditions which produce HFC-245fa.

The cleaning composition of the present invention comprises a sufficient concentration of a suitable HFC, or combination of HFCs, to impart the aforementioned properties to the cleaning composition. For example, if the composition also comprises a flammable material, such as hexane, a sufficient amount of HFC should be present such that the composition has no flash point up to its approximate boiling point. One skilled in the art can readily determine the amount of HFC needed in the composition to achieve a combination of the aforementioned properties. Generally, the composition will contain from about 70% to about 100% by weight of HFC.

In addition to the HFC, the composition may comprise a secondary solvent for aid in dissolving the lubricants or other soils found in vapor compression systems. Such solvents are known in the art. In general, organic solvents, such as hydrocarbons, alcohols, esters and ketones, are preferred. Oxygen- or nitrogen-
5 containing solvents are particularly well suited for dissolving polar materials such as solder flux, while hydrocarbons such as hexanes are well suited for dissolving mineral oil.

The amount of secondary solvent used should be sufficient to provide the composition with a desired solvency for a particular soil to be removed. One
10 skilled in the art can determine readily this amount which generally will range from about 1% to about 30%, and more typically from about 1% to about 10% by weight of the composition.

The HFC-based cleaning composition can be used to clean a variety of types of lubricants used in vapor compression systems. Examples of widely used
15 lubricants are polyalkylene glycols, polyol ester oils, and mineral oils. An example of a polyalkylene glycol oil is Pyroil RL244™ sold by Union Carbide for use with air conditioning systems. Mobil EAL22 sold by Castrol and Lubrikuhl 130 sold by Lubrizol are exemplary of ester oils. An example of a mineral oil is Ford YN-9, which is used in Ford automotive compressors, and BVM 100 oil, which is also
20 used for automotive compressors. Mineral oils are typically used in CFC and HCFC compression systems, which, as discussed above, are being phased out.

In use, the cleaning composition of the present invention is first applied to the surface of a component of the lubricated vapor compression system. The application techniques are known in the art, and include exposing the composition,
25 in either vapor or liquid form, to the component or system. Next, the cleaning composition is removed from the component or system by allowing it to vaporize.

Allowing the composition to vaporize may involve passively waiting until the composition evaporates, or it may involve proactive steps to facilitate vaporization.

Generally, it is preferable to have a composition that remains a liquid at room temperature, but requires just a small change in conditions to vaporize.

5 Techniques for facilitating vaporization are known in the art and include, for example, heating the composition, lowering pressure, driving the vapor/liquid equilibrium of the composition in favor of vaporizing by displacing its vapor with an inert gas or by otherwise providing an environment in which the cleaning composition vaporizes.

10 Suitable cleaning techniques include decreasing a particular component or flushing the system. Degreasing particular components can be performed in an open or closed degreasers. Such cleaning apparatus is well known in the art. An example of a suitable closed type degreasers is the Baron Blakeslee NZE machine (Chicago, IL). In a simple degreaser, the HFC cleaning composition is boiled in a
15 vessel. A cooling coil is positioned above the vessel to condense the vapor of the HFC and other vaporized materials, if any. The soiled component is dipped into the boiling composition for a period of time, for example, about 1 minute, and then suspended in HFC vapor for a period of time, for example, about 1 minute. Alternatively, instead of exposing the component to the vapor, it may be sprayed
20 with unused cleaning composition. Other variations of cleaning cycles that can be used with degreasers can be used in the practice of the present invention.

Like degreasing, various procedures used for flushing the compressor are well known in the art. Basically, the compressor is flushed by pumping the cleaning composition through the compressor or entire vapor compression system.
25 After the compressor or system is flushed, the volatile cleaning composition can be removed from the compressor by blowing nitrogen gas, or other gas, through the compressor or by attaching a vacuum pump to the compressor and drawing a

vacuum on the system. Other suitable cleaning procedures can also be used to contact the cleaning composition of the present invention with the surfaces to be cleaned.

The following examples are illustrative of the practice of the present invention.

5

EXAMPLES

Example 1

This example illustrates the miscibility of hydrofluorocarbons (HFC) with lubricants typically used in vapor compression systems. The miscibility of each of HFC-245fa, HFC-245ea, HFC-356mcfq, and HFC236ca was tested individually with each of the following lubricants: Ford YN-9; Pyroil; Mobil EAL22; and Lubrikuhl. This test was conducted by placing the lubricants and the hydrofluorocarbons in a vessel at room temperature and observing if the mixture has one phase or two phases. The results are shown in Table 2. The use of the term "miscible" in Table 2 means that the mixture of hydrofluorocarbon and lubricant was one phase.

10

15

Table 2 - MISCIBILITY

Lubricant	Solvent	Result
Ford YN-9	HFC-245fa	Cloudy, 2 phases
Pyroil	HFC-245fa	Miscible
Mobil Eal22	HFC-245fa	Miscible
Lubrikuhl	HFC-245fa	Miscible
Ford YN-9	HFC-245ea	Cloudy, 2 phases
Pyroil	HFC-245ea	Miscible
Mobil Eal22	HFC-245ea	Miscible
Lubrikuhl	HFC-245ea	Miscible
Ford YN-9	HFC356mcfq	Cloudy, 2 phases
Pyroil	HFC356mcfq	Miscible
Mobil Eal22	HFC356mcfq	Miscible
Lubrikuhl	HFC356mcfq	Miscible
Ford YN-9	HFC-236ca	Cloudy, 2 phases
Pyroil	HFC-236ca	Miscible
Mobil Eal22	HFC-236ca	Miscible
Lubrikuhl	HFC-236ca	Miscible

The results of miscibility tests for HFCs and air conditioning lubricants indicate that the lubricants were at least partially miscible in all the HFCs tested.

- 5 Furthermore, the complete miscibility of the HFC-245fa, HFC-245ea, HFC-356 mcfq and HFC-236ca with the two ester lubricants, Lubrikuhl 130 and Mobil EAL22, and with the polyalkylene glycol, Pyroil shows their effectiveness as cleaning compositions for vapor compression systems.

Example 2

This example illustrates the cleaning of parts of an air conditioning system. Such cleaning may be required during assembly or service. Instead of using actual parts of an air condition system, stainless steel coupons were used. These coupons first were cleaned and weighed. The coupons were 7.6cm long and 1.1 cm wide. In test #1, they were then dipped in a lubricant. In order to remove the lubricant from the surface of the coupon, a simple degreaser was used. Boiling HFC-245fa was contained in metal beaker of volume 1000 cc. Above the beaker, there was a cooling coil to condense the vapor of the HFC-245fa. After being dipped in the lubricant, the coupon was put into the boiling HFC-245fa for 1 minute and then suspended in HFC-245fa vapor for 1 minute. To expose the coupons to vapor, the coupons were held in the region of the cooling coil where the vapor was condensing. In test # 2, the coupon was dipped into boiling HFC-245fa, and sprayed with clean HFC-245fa. The results of this test are shown in TABLE 3.

TABLE 3

Lubricant	Castrol SW 32	Mineral Oil	Lubrikuhl	Pyroil RL-244
Weight (g) of clean coupon	4.99535	5.03533	5.00839	4.89974
Weight (g) of remaining lubricant after cleaning - Test 1	0.00066	0.0041	0.00008	0.00010
Weight (g) of remaining lubricant after cleaning - Test 2	0.00009	0.00027	0.00007	0.00002

In all these tests, the coupons were satisfactorily cleaned by the HFC-245fa.

Example 3

This example illustrates the effectiveness of HFC as a cleaning composition for vapor compression systems. One test of the efficiency of a flushing fluid is to determine if the fluid can remove most of the oil from a compressor. A Harrison 100T air conditioning compressor was used in this test. The mineral oil was

drained from the compressor and the compressor was washed with hexane. The compressor was then weighed and filled with 205 grams of mineral oil. The oil was drained from the compressor and the compressor was flushed with HFC-245fa. Gaseous nitrogen was then used to remove the volatile HEC-245fa from the compressor. The HFC-245fa vapor was trapped in a dry ice trap. When the compressor was weighed, it was found that it still contained 13 grams of mineral oil. This meant that 94 % of the oil was removed by the procedure. A repeat of the procedure resulted in the removal of 93 % of the remaining oil. These results confirm the ability of an HFC cleaning composition to perform as a flushing agent.

WHAT IS CLAIMED IS:

1. A method for cleaning a component of a vapor compression system, comprising the steps of:

applying a cleaning composition comprising a hydrofluorocarbon to a component of a vapor compression system; and

allowing the cleaning composition to evaporate from the component.
2. The method of Claim 1, wherein the cleaning composition is non-flammable up to its approximate boiling point.
3. The method of Claim 1, wherein the evaporation index for the hydrofluorocarbon ranges from about 1,000 to about 20,000.
4. The method of Claim 1, wherein the hydrofluorocarbon is selected from the group consisting of tetrafluoropropanes, pentafluoropropanes, hexafluoropropanes, hexafluorobutanes and heptafluorobutanes.
5. The method of Claim 4, wherein the hydrofluorocarbon is a hydrofluoropropane selected from the group consisting of 1,1,2,2,3-pentafluoropropane, 1,1,2,3,3-pentafluoropropane, 1,1,1,2,3-pentafluoropropane, 1,1,1,3-pentafluoropropane, and 1,1,1,3-tetrafluoropropane.
6. The method of Claim 1, wherein the composition has a secondary solvent.
7. A composition for cleaning a component of a lubricated vapor compression system, the composition comprising a hydrofluorocarbon and having:

sufficient solvency such that a lubricant selected from the group consisting of polyalkylene glycol, polyol ester, mineral oil, their families and combinations of two or more thereof is at least partially miscible in the composition;
8. The composition of Claim 7, wherein the hydrofluorocarbon has an evaporation rate ranging from about 1,000 to about 20,000.
9. The composition of Claim 8, wherein the hydrofluorocarbon is selected from the group consisting of tetrafluoropropanes, pentafluoropropanes, hexafluoropropanes, hexafluorobutanes and heptafluorobutanes.
10. The composition of Claim 7, wherein the composition has a secondary solvent selected from the group consisting of hydrocarbon solvents, alcohols, esters and ketones, their families and combinations of two or more thereof.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 98/13480

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D C23G F25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 275 669 A (VAN DER PUY MICHAEL ET AL) 4 January 1994 see column 6, line 59 - column 7, line 7; claims	1-4, 7-9
A	US 5 174 906 A (HENRY RICHARD G) 29 December 1992 see claims	1-10
A	US 5 536 327 A (KAISER ROBERT) 16 July 1996 see claim 1	1
A	US 5 375 426 A (BURGENER DAVID) 27 December 1994 see claims	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 September 1998

Date of mailing of the international search report

30/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/13480

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5275669	A	04-01-1994	US 5298083 A	29-03-1994
US 5174906	A	29-12-1992	NONE	
US 5536327	A	16-07-1996	NONE	
US 5375426	A	27-12-1994	NONE	